

Ring crystallizer method and apparatus

Background of the invention

The invention relates to a crystallization method for forming crystals of a substance in a solution, a suspension, or a mixture of liquids, in particular ice crystals from an aqueous solution or organic crystals from an organic melt, the method comprising the steps of:

- crystallizing the solution to form a crystal slurry by means of cooling in a heat exchanger; and
- feeding the crystal slurry from an outflow side of the heat exchanger to an inflow side of the heat exchanger via a recirculation duct and separating at least a part of the crystals from the liquid, characterized in that a recirculation pump is included in the recirculation duct wherein the slurry is continuously supplied through the recirculation duct such that the crystals are homogeneously distributed in the duct and the heat exchanger and such that the under cooling at the outlet of the heat exchanger is the equilibrium temperature T_{eq} minus 0.5 to 0.9 times the meta-stable region ΔT_{max} .

The invention further relates to a crystallizer assembly for use in the method.

The performance of a suspension based crystallization process is typically limited by the step where the pure crystals are physically separated from the impurity containing liquid phase. Wash columns are used for applications where a perfect crystal liquid separation is required. Typical technical examples are the freeze concentration of liquid foods where no aromas and other valuable substances are lost with the ice crystals or the ultra-purification of organic melts where impurity components are perfectly separated from the pure organic crystals. Uniform crystal size distribution and a minimum crystal size of about 100 μm – 200 μm are named in the state of the art as precondition for operation of a wash column and consequently a lot of effort is put in optimizing the upstream suspension crystallization process.

The freeze concentration (FC) process which is described in e.g. US patent No. 4,004,886 is a proven technique for the concentration of liquid food products (e.g. beer, wine, coffee extracts, fruit- and vegetable juices, aroma extracts and the like) as well as specific waste waters, biochemical, pharmaceutical and other aqueous solutions. In this FC process the concept of separate nucleation and growth (SNG) is applied. This SNG process is characterized in that a crystal free liquid is pumped into a scraped surface heat exchanger (SSHE) where small nuclei are formed. These nuclei are then fed to a homogeneously mixed ripening vessel. There the adiabatic ripening conditions allow for gentle, close to equilibrium and thus almost perfect crystal growth and finally results in

spherical crystals with an average particle size of about 300 μm – 800 μm and a narrow crystal size distribution.

The main disadvantages of this SNG process are its complex design with the related high investment costs, a large necessary power input and certain disadvantages which are inherent to a filter application. The design complexity is caused to a large extent by the need to equip the vessel with a sophisticated mixing device and a special scraped filter to allow for the crystal-free feed to the SSHE. The pressure drop over this filter requires the vessel to be designed according to the relevant pressure regulations.

The complexity of design also holds for the SSHE since the SNG concept requires the production of fine nuclei. The design is specific in that it allows for a very small gap between the outer shell of the SSHE and the inner rotor in the range of several mm only. In this way extremely short residence times with the corresponding high under cooling are achieved. These conditions provide for the required small crystal size. The manufacturing of the SSHE has to follow very accurate mechanical tolerances to assure perfect centering of the rotor, especially for larger units. Deviations will cause mal-distribution of product around the circumference of the SSHE.

Another shortcoming of the SNG concept is the fact that the filter requires remarkable efforts for cleaning in its application for sanitary design.

In EP 948 984 a crystallization method is proposed where nucleation and growth takes place at the same time in just one scraped surface drum crystallizer. A disadvantage of this method is that it still requires the use of a filter for discharge of the mother liquor with essentially the same drawbacks as described above for the SNG concept. A further disadvantage of this method is the fact that the surface area for heat exchange and the volume of the vessel are linked with each other by geometrical relations. Usually the volume of a crystallizer vessel is determined by the need for a certain residence time. In a crystallizer design according to EP 948 984 the size of the scraped surface drum crystallizer is always governed by the required surface area for the heat exchange. The drum crystallizer, which represents a pressure vessel, will thus have to be built much larger than principally required with respect to residence time.

The object of the present invention is to provide a method for the production of solids in a liquid by crystallization, which method does not have the disadvantages mentioned above, or at least to a substantially reduced amount. It is a further object of the present invention to provide a crystallization apparatus of low complexity, relatively low power input and which is easily cleaned. It is again an object of the present invention to provide a crystallization method, which is feasible to produce crystals that are suitable to be separated in a wash column.

The present invention is characterized by a recirculation pump that is included in a recirculation duct, wherein the slurry is continuously supplied through the

recirculation duct from an outflow side of a heat exchanger to the inflow side of the same heat exchanger such that the under cooling at the outlet of the heat exchanger is continuously decreased during the cycle and transferred into crystal growth, until it's lowest value is reached shortly before re-entering the heat exchanger. This results in a cyclic pattern of under cooling. The under cooling at the outlet of the heat exchanger shall be the equilibrium temperature minus 0.5 to 0.9 times the meta-stable region (ΔT_{\max}) of the crystallizing substance and at the inlet of the heat exchanger this under cooling shall be reduced to the equilibrium temperature minus 0 to 0.3 times the meta-stable region of the crystallizing substance.

10 The term equilibrium temperature T_{eq} as is used herein, means the temperature at which the solid phase and the liquid phase of a solution of a certain concentration are at equilibrium. The meta-stable region, ΔT_{\max} , is the difference between the equilibrium temperature of a solution and the temperature at which nucleation occurs.

It has been unexpectedly found that this simple setup is suitable to produce
15 crystals of sufficient size having a comparable narrow size distribution at a lower residence time, which can be subsequently effectively separated.

In particular it was found that wash columns as, e.g. described in US patent No. 3,872,009 (piston wash column), in US patent No. 4,481,169 (screw type wash column) or in US patent No. 4,734,102 (hydraulic wash column) can be operated with crystals
20 which are less perfect than those produced in the concept of separate nucleation and growth.

Said recirculation duct is forming a closed duct of such a diameter and length, so as to providing sufficient volume and therefore residence time for the crystals to grow. The duct diameter shall be adjusted such that at a given flow rate, the flow
25 velocity in the duct is between 0.2 m/s and 3 m/s and preferably between 0.5 m/s and 1.5 m/s to prevent back-mixing and settling or floating of the crystals. The larger the difference between crystal and fluid density the higher the required fluid velocity shall be chosen. If this difference exceeds 300 kg/m³ the velocity should be higher than 0.5 m/s. Usually the duct diameter is between 100 mm and 2000 mm while the length is
30 between 10 m and 100 m and preferably between 15 m and 30 m. The orientation of the straight duct sections of the recirculation duct could be either vertically or horizontally. The vertical configuration is preferably limited to two straight duct sections, which are connected with large radius bends to form a closed loop. Additional crystallizer volume can be generated by extending the vertical pipelines to larger diameters. The horizontal
35 configuration is preferably used for applications where the total duct length exceeds 20

m. In this configuration the total duct length is split into sections of straight pipes – each with a length of about 4 m to 12 m – which again are connected with large radius bends to form a winded closed loop. The horizontal ducts can be mounted with a slight slope (e.g. 2 %) to allow for complete emptying of the crystallizer.

- 5 The mass flow rate ($\dot{m}_{circ.}$) in the recirculation duct is given by an energy balance for the heat exchanger and the requirement that the temperature difference (ΔT) between the inlet and the outlet of the heat exchanger must not exceed the meta-stable region ($\Delta T_{max.}$).

10
$$\dot{Q}_{cool} + \dot{Q}_{cryst.} + \dot{Q}_{loss} = \dot{m}^* c_{p,l} * \Delta T$$

\dot{Q}_{cool} is the energy flux for cooling

$\dot{Q}_{cryst.}$ is the energy flux for crystallization

\dot{Q}_{loss} is the energy loss

\dot{m}^* is the mass flow rate in the recirculation duct

- 15 $c_{p,l}$ is the specific heat of the crystals suspension

In total the energy for cooling (\dot{Q}_{cool}), for crystallization ($\dot{Q}_{cryst.}$) and for compensation of losses (\dot{Q}_{loss}) has to be transported through the heat transfer surface of the heat exchanger and results in a temperature decrease of the recirculating suspension.

20
$$\frac{\dot{m}_{circ.}}{\dot{m}_{cryst.}} = (\eta_{cool} + \eta_{loss} + 1) * \frac{\Delta h}{c_{p,l} * \Delta T}$$

η_{cool} & η_{loss} are determined by the following

equation $\eta_{cool} = \left(\frac{\dot{Q}_{cool}}{\dot{Q}_{cryst.}} \right), \eta_{loss} = \left(\frac{\dot{Q}_{loss}}{\dot{Q}_{cryst.}} \right).$

This actual ΔT is influenced by the specific heat of the suspension ($c_{p,l}$) and especially by the specific mass flow rate of the suspension ($\frac{\dot{m}_{circ.}}{\dot{m}_{cryst.}}$).

In the crystallization method according to the present invention, no filter or separator is included in a recirculation path between the outlet of the heat exchanger and the inlet of the heat exchanger. This results in a high through put and a low pressure drop across the recirculation duct and hence in low energy consumption.

5 According to a preferred embodiment of the present invention a SSHE is used as heat exchanger. The SSHE has a jacketed outer shell for supply of the cooling and a rotating central axis with knives attached to prevent the heat exchanger surface from plugging. The annular zone between the inner rotor and the outer shell does not require the narrow gap with the corresponding high mechanical tolerances like in the
10 conventional SNG process, but extends for 15 mm at least and preferably extends to between 0.1 and 0.4 times the outer diameter of the heat exchanger. At values lower than 15 mm, problems with slurry blockage, pressure build-up and uneven flow distribution can occur. Depending on the viscosity and slurry density of the crystallizing fluid specific heat flux ratios between $10,000 \text{ W/m}^2$ and $25,000 \text{ W/m}^2$ are
15 achieved. It was found that a low heat transfer coefficient can be compensated to a certain extent by a higher temperature difference over the SSHE.

To allow for reliable long term operation, the SSHE can be supplied with a specifically designed outlet head. The design of the outlet head is such that it allows for a smooth transition of the suspension velocity from the inside of the SSHE to the
20 outflow of the SSHE. Preferably the suspension velocity stays constant and most preferably the velocity increases towards the outflow of the SSHE. In this configuration it was found that blockage of the outlet of the SSHE with crystals can reliably be prevented. Without such novel outlet head blockage has frequently been observed after exceeding an operation time of about 8 hours.

25 Generally large volume flow rates between $100 \text{ m}^3/\text{h}$ and $6000 \text{ m}^3/\text{h}$ are required to limit the maximum under cooling in the ring crystallizer. Since the crystals pass the re-circulation pump in the crystallization duct about 100 to 2000 times before they are discharged from the crystallizer, special attention has to be paid to limit crystal breakage in these pumps. The pressure drop in the crystallization duct is generally
30 limited to figures below 0.7 bar and frequently below 0.2 to 0.4 bar. For these flow conditions the application of axial flow pumps, which are commercially available by e.g. Allweiler, Klaus Union and KSB, is recommended. The impeller of the recirculation pump shall run at a tip speed of below 15 m/s and more preferably below 12 m/s.

35 The ring crystallizer should be operated at a slurry concentration of between 10 wt% and 40 wt% and more preferably between 25 wt% and 30 wt%. With these crystal concentrations there will be sufficient crystals at all places within the crystallizer to transform the under cooling into crystal growth and thus to limit the under cooling to an

allowable value within the meta-stable region. In this way primary nucleation is prevented. For a given crystallizer volume high slurry densities lead to the presence of a large number of crystals in the ring crystallizer. Since crystals are discharged at a given rate the individual crystal will remain for a longer period in the crystallizer.

5 In a further embodiment of the invention and in case a SSHE is used as heat exchanger, it can be contemplated to use two different pumps in order to uncouple the relevant flow regimes in the crystallization duct and in the heat exchanger. Since the maximum heat exchanger surface of a single SSHE is limited to about 12 m², larger capacities can be realized by arranging more SSHE's in a parallel configuration. Such a process scheme has the additional advantage that in case a heat exchanger needs to be
10 molten down, the process can be continued with the remaining heat exchangers staying in operation. It is also possible to proactively melt down the heat exchangers in a cyclic pattern according to a predefined schedule to preventively avoid blockage at all.

In general the method of the present invention produces slightly smaller crystals
15 than the conventional separate nucleation and growth (SNG) process but surprisingly it has been found that the difference in crystal size is not very pronounced. Ice crystals that are produced according to the crystallization method of the present invention have a spherical shape. Their diameter is generally below 900 µm. The average particle size has been found to depend on the concentration of the soluble substance. For 5 wt% the
20 particle size is generally between 300 µm and 500 µm; it decreases to values between 200 µm and 400 µm at 20 wt% and further decreases to values between 150 µm and 350 µm at 40 wt%. At 50 wt% the particle size is found to be between 100 µm and 200 µm.

In another embodiment of the present invention it can be contemplated to use a
25 shell & tube heat exchanger (S&T HE) as heat exchanging device. Since ice crystals, as well as organic crystals are very sensitive with respect to the formation of encrustations this configuration can only be run continuously if

- (i) The specific heat flux through the heat exchanger wall is limited to below 1000 W/m² and preferably to below 500 W/m².
- 30 (ii) The specific mass flow rate in the recirculation duct per kg of crystallized substance is about 50 to 300 times the reciprocal of the meta-stable region ($1/\Delta T_{\max}$) and preferably about 100 to 150 times the reciprocal of the meta-stable region.
- (iii) The velocity in the heat exchanger pipes is above 1.5 m/s and preferably above
35 1.8 m/s.
- (iv) The suspension density is as high as possible but at least above 10 wt%.

The total cooling load which is transported through the heat transfer surface is to a large amount directly transformed into crystal growth. These crystals are then

periodically scraped off from the heat exchanger wall. Which causes the resulting under cooling of the liquid to be much lower than in a configuration with a S&T HE. This is the reason why a ring crystallizer with a SSHE can be operated at recirculation rates that are 2 to 6 times lower than in its application with a S&T HE.

5 Organic crystals that are produced according to the crystallization method of the present invention frequently have a monoclinic or an orthorombic crystal structure. The relation of the dimensions length : height : width of the above structures is often according to the following ratios: 1 ... 10 : 1 ... 2 : 1. The length of the crystals is frequently between 100 μm and 1000 μm , commonly between 200 μm and 600 μm .

10 The produced crystals could be separated by all means of known mechanical separation devices, like centrifuges, filters and the like. Since it has been unexpectedly found that the crystal quality is also good enough to allow for a complete separation of the produced crystals on a wash column, this separation process is included in the present invention as preferred crystal liquid separator. Since the piston type wash
15 column is the least sensitive one with respect to quality of the feed crystals in terms of crystal size and crystal size distribution, this wash column is the preferred type in combination with the crystallization process of the present invention.

 The invention is not only directed to the crystallization method as such, but also to the use thereof for concentrating aqueous solutions and purifying organic melts. The
20 crystallization method of the present invention can be combined with a packed bed wash column for the separation of the pure crystals.

 In general the crystallization method of the present invention is suitable for concentrating liquid foods such as coffee, beer, wine, vinegar, fruit juices, citrus juices, vegetable juices, fish extract, seafood extract, meat extract, herb extracts, aroma
25 extracts and the like, for the desalination of sea water or for concentrating waste waters and other aqueous solutions such as aqueous pharmaceutical or bio-chemical solutions and the like.

 More in particular the crystallization method of the present invention could also be used for the crystallization of organic melts, such as acrylic acid, acetic acid,
30 benzoic acid caprolactam, cresol, maleic acid, MDI, monochloroacetic acid, m-Xylene, naphthalene, p-DCB, p-NCB, p-Xylene, phenol, TDI, and the like .

Brief description of the drawings

 The invention will be described in detail with reference to the accompanying drawings, wherein:

35 Fig. 1 is a phase diagram of a mixture of substances A and B, showing the equilibrium temperature and the meta-stable region (ΔT_{max});

Fig. 2 is a schematic temperature versus time diagram of the under cooling realized at the outlet of the heat exchanger and the subsequent loss of this under cooling in the recirculation duct ;

Fig. 3 is a schematic drawing of a ring crystallizer with a scraped surface heat exchanger (SSHE) and a wash column as crystal-liquid separator, according to the present invention;

Fig. 4 is a cross-sectional view of a prior art SSHE;

Fig. 5 is a cross-sectional view of the SSHE according to Fig. 3 along the line V-V;

Fig. 6 is a longitudinal cross-sectional view of the outlet side of SSHE of Fig. 3;

Fig. 7 is a schematic drawing of another preferred embodiment of the process according to the invention where a separate pump is used for supply of the SSHE with the aim to uncouple flow regimes in the ring crystallizer and in the SSHE;

Fig. 8 is a schematic drawing of a modification of the process according to Fig. 7 where various parallel SSHE's are arranged with one ring crystallizer for easy scale up purposes; and

Fig. 9 is a schematic drawing of a ring crystallizer with a shell & tube heat exchanger (S&T HE) as heat exchanger device and a wash column as crystal-liquid separator.

20 Description of the detailed embodiment

Fig. 1 is a phase diagram, giving temperature versus concentration of a mixture of substances A and B. At the equilibrium temperature, T_{eq} , pure substance B is in equilibrium in a liquid mixture with X_{eq} weight percent of B. The meta stable region ΔT_{max} is the temperature range below the equilibrium temperature in which no spontaneous nucleation of crystals occurs.

Fig. 2 shows the cyclic undercooling in the heat exchanger and recirculation duct of the crystalliser assembly of the present invention, as described in Figs. 3, 7, 8 and 9. In heat exchanger the crystal slurry is rapidly cooled to 0.5-0.9 times the meta stable region ΔT_{max} , whereas in the recirculation duct, the temperature of the crystal slurry more slowly rises to the equilibrium temperature minus 0-0.3 the meta stable region ΔT_{max} .

Fig. 3 shows a crystalliser assembly 1 with a scraped surface heat exchanger 2. The outlet 4 of the heat exchanger 2 is connected to the inlet 3 via a recirculation duct

5. Recirculation pump 6 recirculates slurry from the outlet 4 to the inlet 5. Through feed line 12 the mixture of substances is supplied to the crystalliser assembly 1. Through line 7 the crystal slurry is transported to a separator 8. Crystals are removed via discharge line 9, whereas the concentrate may be removed via discharge line 10, whereas the remainder of the solution may be recirculated back to the heat exchanger 2 via line 11.

Fig. 4 shows a surface scraped heat exchanger 20 such as known in the prior art. The heat exchanger is provided with a circular cross-section and comprises a rotor 22, carrying two scraping blades 23,24, scraping the heat exchanger wall 21. The diameter of the rotor 22 is relatively large, leaving a small gap between the wall 21 and the rotor, through which the liquid passes with a relatively large velocity.

Fig. 5 shows the heat exchanger 2 of the present invention. The rotor 32 is of relatively small diameter, for instance leaving a gap 37 of a width between 0.1 and 0.4 times the internal diameter D of the inner wall 31. The scraping blades 33, 34 are mounted on arms 35 on the rotor 32. The heat exchanger 2 of the present invention operates with a slurry mixture instead of clear liquid. A larger gap is required according to the present invention to prevent uneven flow regimes and/or pressure build-up. Such a large gap results in reduced mechanical tolerances and hence reduced costs.

Fig. 6. shows the specially designed outlet head 36 of the heat exchanger according to the present invention. The flow channel 37 between the rotor 32 and the heat exchanging wall 31 connects via a curved section to the outlet 4, without abruptly changing the flow direction or decelerating or stopping the crystal slurry flow. In this way, undesired accumulation of crystals is prevented.

Fig. 7 shows a crystalliser assembly of similar type as shown in Fig. 3, and like parts are indicated with the same reference numerals. In the crystalliser assembly 1 of Fig. 7, an additional loop 15 with second pump 16 are included to form the main circulation loop in which the suspension can be circulated. Smaller amounts of slurry are fed through the heat exchanger 2 to obtain the desired under cooling. The flow through the heat exchanger 2 can be decoupled from the flow through line 15.

Fig. 8 shows a crystalliser assembly of similar type as shown in Fig. 7, with three heat exchangers 2, 2' and 2'' operated in parallel, for increased capacity with standard SSHE.

Fig. 9 finally shows an arrangement in which the crystalliser 2 is formed by a shell and tube heat exchanger, of a type such as described in Handbook of Industrial Crystallization, Allen S. Myerson, page 121, Butterworth Heineman 1993.

The following examples are intended only to further illustrate the invention and are not intended to limit the scope of the invention, which is defined by the claims.

EXAMPLE 1

A sugar solution of 17 wt% was concentrated by the formation of ice crystals using the apparatus and arrangement as schematically shown in Fig. 3.

The 17 wt% sugar solution was supplied to the ring crystallizer at a rate of approximately 12 kg/h where it was mixed with crystal slurry being recirculated in the duct at a recirculation rate of approximately 30 m³/h. The ring crystallizer was sized to hold approx. 50 l of crystal-liquor suspension. The duct had a diameter of 80 mm and a total length of approx. 10 m. The ice slurry density in the duct was approximately 20 wt% and the slurry velocity was about 1.7 m/s. The heat exchanger had an effective heat exchange surface of 0.28 m² and the temperature difference between the solution and the cooling medium was kept at approximately 8 K resulting in a heat flux of about 10,000 W/m². 35 kg/h of the ice suspension were continuously removed from the ring crystallizer via line 7 to the wash column B. The ice crystals were separated from the liquor and discharged from the process through line 9 as pure water at a rate of 7 kg/h. A 40 wt% concentrated sugar product flow of 5 kg/h was discharged through line 10, while the remainder of the sugar solution (23 kg/h) was recycled back to the ring crystallizer via line 11. The spherical ice crystals which were obtained had an average size of 250 µm.

EXAMPLE 2

A sugar solution of 5 wt% was concentrated by the formation of ice crystals using the apparatus and arrangement as schematically shown in Fig. 8.

The sugar solution was supplied to the ring crystallizer at a rate of 17 kg/h where it was mixed with crystal slurry being recirculated in the duct at a recirculation rate of approximately 30 m³/h. The ring crystallizer was sized to hold approx. 70 l of crystal-liquor suspension. It was composed of one straight duct of 6 m length and a double-pipe heat exchanger of the same length which were connected by bends with each other to form one closed loop. The duct had a diameter of 80 mm and a total length of approx. 14 m. The ice slurry density in the duct was approximately 15 wt% and the slurry velocity was about 1.7 m/s. The heat exchanger had an effective heat exchange surface of 1.5 m² and the temperature difference between the solution and the cooling medium was kept at approximately 1.5 K resulting in a heat flux of about 500 W/m². 17 kg/h of the ice suspension were continuously removed from the ring crystallizer containing approx. 2.5 kg/h of ice crystals. The crystals had the same

spherical shape as produced in the process of Example 1 and an average size of 500 μm .

EXAMPLE 3

5 A sugar solution of 14 wt% was concentrated by the formation of ice crystals using the apparatus and arrangement as schematically shown in Fig. 7.

10 The 14 wt% sugar solution was supplied to the ring crystallizer at a rate of 560 kg/h where it was mixed with crystal slurry being recirculated in the duct at a recirculation rate of approximately 95 m^3/h . The ring crystallizer was sized to hold approx. 880 l of crystal-liquor suspension. It was composed of 8 straight ducts of 6 m length which were connected by large radius bends with each other to form one closed loop. The duct had a diameter of 150 mm and a total length of approx. 50 m. The ice slurry density in the duct was approximately 25 wt% and the slurry velocity was about 1.5 m/s. From the ring crystallizer approx. 8 m^3/h of crystal liquor suspension were supplied to the scraped surface heat exchanger. The heat exchanger had an effective
15 heat exchange surface of 1.68 m^2 and the temperature difference between the solution and the cooling medium was kept at approximately 12 K resulting in a heat flux of about 23,000 W/m^2 . 1200 kg/h of the ice suspension were continuously removed from the ring crystallizer via line 7 to the wash column B. The ice crystals were separated from the liquor and discharged from the process through line 9 as pure water at a rate of
20 300 kg/h. A 30 wt% concentrated sugar product flow of 260 kg/h was discharged through line 10, while the remainder of the sugar solution (640 kg/h) was recycled back to the ring crystallizer via line 11. The product crystals which were obtained had an average size of 350 μm and were virtually spherical in shape.